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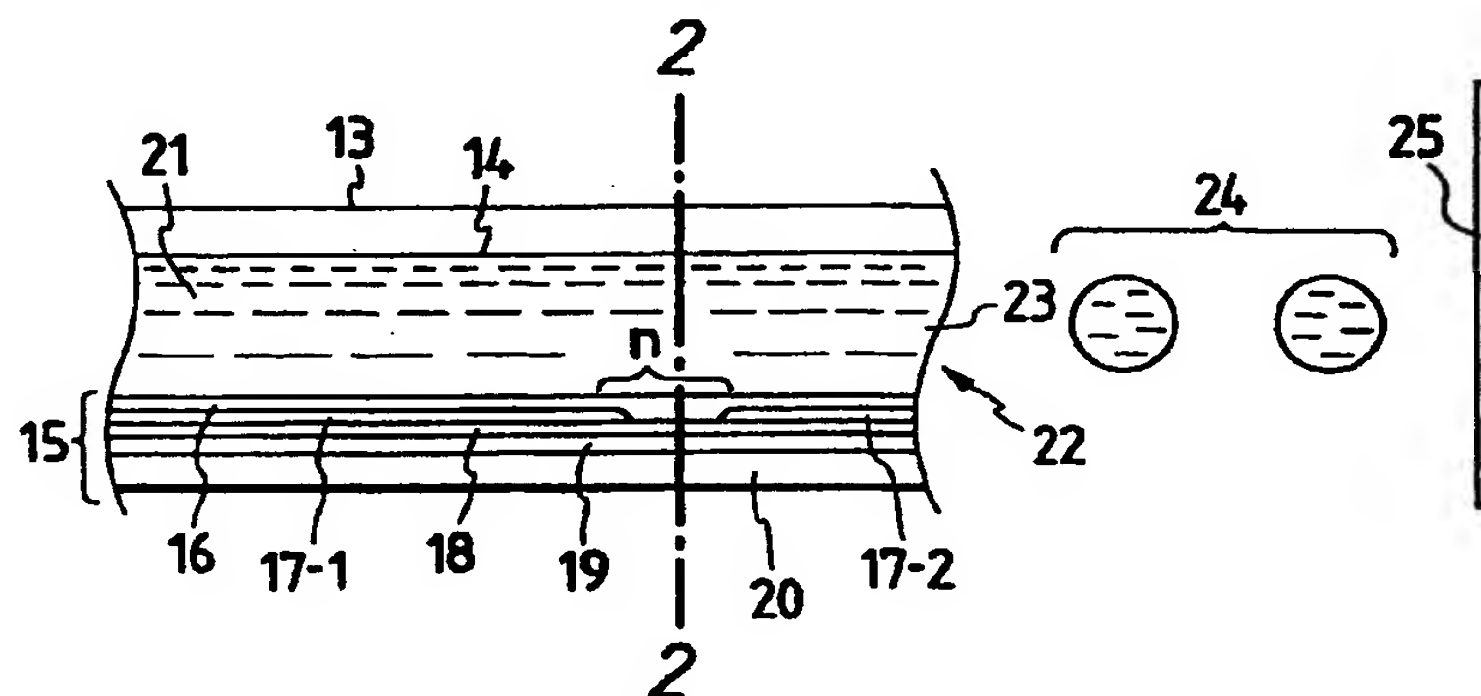
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(54) Printing medium and its use using inkjet printing method

(57) Disclosed herein is a printing medium comprising a surface layer having liquid permeability and an ink-retaining layer, wherein a pore volume of pores corresponding to a peak not greater than 100 nm in a pore diameter distribution curve of the printing medium is at

most 0.015 cc/g, a pore volume of pores corresponding to at least one of peaks greater than 100 nm is at least 0.015 cc/g, and the pH of the surface layer is at least 8.

FIG. 1



EP 0 743 193 A1

## Description

BACKGROUND OF THE INVENTION5 Field of the Invention

The present invention relates to a printing medium which has excellent ink absorbency and provides an image excellent in coloring, gloss and fastness properties, a printing method using such a printing medium, and a method of producing a print.

10

Related Background Art

Ink-jet printing systems have attracted attention because of ready attainment of high-speed, full-color and high-density printing. Printing apparatus making good use of an ink-jet printing system have also spread. As printing paper applied to such an ink-jet printing system, may be mentioned exclusive coated paper described in, for example, Japanese Patent Application Laid-Open No. 59-35977.

Since such exclusive coated paper is however so constructed that a printing agent in an ink is retained on the surface of its absorbing layer as much as possible because an image formed on the paper is viewed from the side of the printing surface thereof, it involves a drawback that the resultant image becomes poor in durability such as water fastness, and storability. In order to improve printability such as ink absorbency, coloring ability of the printing agent, and the quality, resolution, coloration, optical density and gloss of an image printed, there has thus been proposed a printing medium as described in Japanese Patent Application Laid-Open No. 62-140878, wherein a printing surface and a viewing surface are different from each other. This printing medium is constructed by laminating an ink-retaining layer and a porous surface layer on a transparent base material. Printing is conducted from the surface layer side, and an image printed is viewed from the base material side.

In the ink-jet printing system, various water-soluble dyes are separately dissolved in water or a liquid mixture of water and an organic solvent, and the resultant solutions are used as inks. However, the inks using such a water-soluble dye often offer a problem that the resulting image becomes poor in light fastness because these water-soluble dyes have poor light fastness per se.

Besides, such inks are water-soluble, so that the water fastness of the image printed also often becomes a problem. Namely, when the printed image is exposed to the rain or splashed with sweat or drinking water, the image may become blurred or faded.

On the other hand, the same problems arise even on writing utensils using a dye, such as ballpoint pens. In order to solve the problems of light fastness and water fastness, there have thus been proposed various water-based pigment inks for writing utensils. As examples in which investigations are made as to dispersion stability, prevention of solidification of ink at a penpoint or prevention of wear of a ball point in a ballpoint pen for putting water-based pigment inks to practical use, there are mentioned Japanese Patent Application Laid-Open Nos. 58-80368, 61-200182, 61-247774, 61-272278, 62-568, 62-101671, 62-101672, 1-249869 and 1-301760. Ballpoint pens and markers using a water-based pigment ink have recently come to be marketed as commercial products. As ink-jet inks using a water-based pigment ink, pigment inks using a specific water-soluble solvent and a polymeric dispersant have been proposed in Japanese Patent Application Laid-Open Nos. 56-147859 and 56-147860, etc.

As described above, numerous proposals as to pigment inks for ink-jet have been made.

With the improvement in performance of ink-jet printing apparatus, such as speeding up of printing and multi-coloring of images, in recent years, printing media for ink-jet are also required to have higher and wider properties. More specifically, they are required to simultaneously satisfy, for example, the following properties:

- (1) causing no color deviation from an inherent color of a dye and being able to achieve proper color mixing;
- (2) having high ink absorptivity (absorbing capacity being great, and absorbing time being short);
- (3) providing dots high in optical density and clear in periphery;
- (4) providing dots having a substantially round shape and a smooth periphery;
- (5) undergoing scarce changes in the properties even at varied temperatures and humidities and no curling;
- (6) undergoing no blocking;
- (7) being able to stably store images formed thereon for a long period of time without deteriorating them (in particular, in a high-temperature and high-humidity environment); and
- (8) being stable without undergoing deterioration even when stored for a long period of time (in particular, in a high-temperature and high-humidity environment).

As described above, it has recently been reported in great numbers to use pigment inks in ink-jet printing with a view toward improving the water fastness and light fastness of an image formed on a printing medium.

When the pigment inks are used for a printing medium in which the printing surface and the viewing surface have an opposite relation to each other as described above, however, a problem that an image formed on the medium becomes low in optical density and poor in coloring upon viewing it from the viewing surface side arises.

## 5 SUMMARY OF THE INVENTION

It is an object of the present invention to provide a printing medium which comprises a printing surface and a viewing surface different from each other, satisfies the above-described properties at the same time in a well-balanced relation, and can provide an image having high optical density and excellent coloring when conducting printing on the printing surface with pigment inks developing fastness properties such as water fastness and light fastness as described above, and viewing the image from the viewing surface side, a printing method using this printing medium, and a method of producing a print.

The above object can be achieved by the present invention described below.

According to the present invention, there is thus provided a printing medium comprising a surface layer having liquid permeability and an ink-retaining layer, wherein a pore volume of pores corresponding to a peak not greater than 100 nm in a pore diameter distribution curve of the printing medium is at most 0.015 cc/g, a pore volume of pores corresponding to at least one of peaks greater than 100 nm is at least 0.015 cc/g, and the pH of the surface layer is at least 8.

According to the present invention, there is also provided a printing process comprising ejecting inks, which each comprise pigment particles having an average particle diameter within a range of from 100 nm to 500 nm, from ejection orifices in response to printing signals to apply the inks in the form of droplets to the printing medium described above.

According to the present invention, there is further provided a process of producing a print, comprising applying inks, which each comprise pigment particles having an average particle diameter within a range of from 100 nm to 500 nm, to the surface layer of the printing medium described above by an ink-jet system, thereby forming an image on the ink-retaining layer through the surface layer.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a longitudinal cross section, taken along the flow path of ink, illustrating an example of the construction of a head of an ink-jet printing apparatus suitable for use in conducting printing on a printing medium according to the present invention.

Fig. 2 is a transverse cross section, taken along line 2-2, of the head shown in Fig. 1.

Fig. 3 is a perspective view of the appearance of an illustrative multi-head.

Fig. 4 illustrates an exemplary ink-jet printing apparatus in which the head has been incorporated.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

A principal feature of the present invention resides in that printing is conducted with inks each comprising, as a principal component of a printing agent, a pigment on a printing medium, in which the printing surface and the viewing surface have an opposite relation to each other, unlike the conventional printing media in which the printing surface is identical with the viewing surface.

More specifically, according to the present invention, the printing is conducted with the inks on the surface layer which is a printing side, and an image printed is viewed from the side of the ink-retaining layer, which is a viewing side.

Accordingly, the surface layer has good liquid permeability, i.e., a function of rapidly absorbing and transmitting the ink applied to the surface thereof.

At this time, the surface layer must have high affinity for a liquid medium in the ink and at the same time have rather low affinity for the pigment as the printing agent, and must be so constructed that the pigment can pass through pores in the surface layer. If the pores are smaller than the particle diameter of the pigment, the pigment cannot pass through the pores and remains on the printing surface side, which causes a problem that an image formed becomes low in optical density and poor in coloring when the image is viewed from the viewing surface side.

Accordingly, the surface layer must be constructed in such a manner that materials which have no properties of wetting, penetration, diffusion and the like to the liquid medium in the ink are selected, and its pores become greater than the particle diameter of the pigment, while the pH of the surface layer must be adjusted to such a moderate pH (within a stable pH region) that the pigment in the ink undergoes no aggregation when the ink passes through the pores in the surface layer.

On the other hand, the ink-retaining layer must have ink absorptivity stronger than the surface layer for the purpose of absorbing and capturing the ink temporarily absorbed in the surface layer therein.

Accordingly, the ink-retaining layer must have high affinity not only for the liquid medium in the ink but also for the printing agent in the ink. It is more preferable that the pH of the ink-retaining layer should fall within a pH region (be lower



than any pH within the stable pH region) in which the pigment in the ink aggregates, because the water fastness and moisture fastness of the resulting image is more improved. The pH of the surface layer or ink-retaining layer in the present invention is a value measured in accordance with the Surface pH Measurement of Paper (J. TAPPI Test Methods for Paper and Pulp, No. 6-A).

The present invention will hereinafter be described in detail on the basis of the embodiments.

The printing medium according to the present invention comprises a base material as a substrate, an ink-retaining layer formed on the substrate and serving to substantially absorb and capture an ink or a printing agent therein, and a surface layer formed on the ink-retaining layer and serving to directly receive the ink and substantially not retain the ink therein. Further, a pore volume of pores corresponding to a peak not greater than 100 nm in a pore diameter distribution curve of the printing medium is at most 0.015 cc/g, and a pore volume of pores corresponding to at least one of peaks greater than 100 nm is at least 0.015 cc/g.

In the above construction, the base material is not always necessary if the surface layer or the ink-retaining layer combines the function as the substrate. Any conventionally known base material may be used as the base material used in the present invention. Specific examples thereof include light-transmitting base materials such as plastic films, sheets or plates composed of polyester resins, diacetate resins, triacetate resins, polystyrene resins, polyethylene resins, polycarbonate resins, polymethacrylate resins, cellophane, celluloid, polyvinyl chloride resins, polyimide resins and the like, and glass sheets or plates.

As described above, an image printed on the printing medium according to the present invention is viewed from a side opposite to the printing side. Therefore, the base material may be subjected to any processing so far as the processed base material retains its good light transmitting properties. For example, it is possible to impart the desired pattern or gloss, for example, moderate gloss or silk-finish pattern to the base material.

It is also possible to impart water resistance, wear resistance and blocking resistance to the base material.

The surface layer making up the printing medium according to the present invention is required to have good liquid permeability.

The term "liquid permeability" as used herein refers to a nature that an ink is rapidly passed through so as substantially not to retain a printing agent in the ink in the surface layer. A preferred embodiment for improving the liquid permeability is to have the surface layer have a porous structure with cracks or communicating pores in the interior of the surface layer.

Since the average particle diameter of pigment particles in an ink to be used in the present invention is generally within a range of from 100 nm to 500 nm, it is also essential that a pore volume of pores corresponding to a peak not greater than 100 nm in a pore diameter distribution curve of the printing medium be at most 0.015 cc/g, and a pore volume of pores corresponding to at least one of peaks greater than 100 nm be at least 0.015 cc/g. If the pore volume of the pores corresponding to the peak not greater than 100 nm is greater than 0.015 cc/g, the pigment particles in the ink are retained in the surface layer, so that an image having sufficient optical density and brightness cannot be formed. Similarly, the diameter of pores corresponding to the peak greater than 100 nm in the pore diameter distribution curve must be greater than the average particle diameter of the pigment particles.

On the other hand, if the pore volume of the pores corresponding to the peak greater than 100 nm is smaller than 0.015 cc/g, the resulting printing medium becomes deteriorated in liquid permeability and can provide only an image lowered in optical density and brightness.

The pore diameter distribution curve referred to in the present invention is determined by the mercury intrusion porosimetry. As an apparatus used in such determination, may be mentioned Porosimeter Poresizer 9320 (trade name, manufactured by Shimadzu Corporation).

Since a reflection image printed is viewed from the opposite side to the printing surface in the present invention as described above, it is preferable that the surface layer have good light diffusing properties.

The surface layer satisfying the above properties is composed principally of resin particles and a binding agent.

As the resin particles used in the present invention, at least one of organic pigments such as thermoplastic resins and thermosetting resins having no adsorptivity to printing agents, for example, powders and emulsions of resins such as polyethylene, polymethacrylates, elastomers, ethylene-vinyl acetate copolymers, styrene-acrylic copolymers, polyesters, polyacrylates and polyvinyl ethers, may be used as desired.

The resin particles used in the present invention are not limited to the above resin particles, and any well-known material may be used so far as it has no adsorptivity to the printing agents.

The preferable particle diameter of the resin particles is within a range of from 0.3 to 20  $\mu\text{m}$ , more preferably from 0.5 to 12  $\mu\text{m}$ . If the particle diameter is smaller than the lower limit of the above range, the penetrability of the pigment particles in the ink becomes insufficient, so that difficulty is encountered on the formation of an image having a sufficient optical density. If the particle diameter is greater than the upper limit of the above range on the other hand, the roundness of dots to be formed on the resulting surface layer tends to be impaired, and so the resulting image gives a rough feeling.

The binding agent used in the present invention has a function of binding the resin particles to each other and/or to the ink-retaining layer and is required to have no adsorptivity to the printing agents like the resin particles.

As a preferable material for the binding agent, any conventionally-known material may be used so far as it has the above function. For example, one or more of resins such as polyvinyl alcohol, acrylic resins, styrene-acrylic copolymers, ethylene-vinyl acetate copolymers, starch, polyvinyl butyral, gelatin, casein, ionomers, gum arabic, carboxymethylcellulose, polyvinyl pyrrolidone, polyacrylamide, phenol resins, melamines, epoxies and styrene-butadiene rubber may be used as desired.

The materials as described above are used to adjust the pH of the surface layer to at least 8, preferably within a range of from 8 to 10. When the pH of the surface layer is lower than 8, the pigment in the ink tends to aggregate in the surface layer, so that the optical density of the resulting image becomes insufficient when viewed from the side of the ink-retaining layer. When the pH is too high on the other hand, the coloring of the resulting image tends to be lowered.

If the desired pH cannot be achieved by only the above materials, various cationic or anionic surfactants, various cationic or anionic polymers or oligomers, and various pH adjustors may be used in combination.

No particular limitation is imposed on such anionic compounds so far as they contain an anionic part in their molecules.

As examples of the anionic surfactants, may be mentioned alkylbenzenesulfonates, salts of alkylsulfates, alkyl-naphthalenesulfonates, alkylphosphates, alkylsulfosuccinates, naphthalenesulfonic acid-formalin condensates and polyoxyethylene alkylphosphates. Amphoteric surfactants such as alkylbetaine, imidazolinium betaine and alanine type surfactants containing an anionic part may also be included.

The anionic polymers or oligomers include those having a sulfonic group, carboxyl group, sulfate group, phosphate group, phenolic hydroxyl group, alcoholic hydroxyl group and/or the like in their molecules. All polymers and oligomers having a sulfonic group, carboxyl group, sulfate group, phosphate group, phenolic hydroxyl group, alcoholic hydroxyl group and/or the like, for example, carboxyl group-terminated polyesters obtained by reacting a polycarboxylic acid with a polyhydric alcohol; acid cellulose derivatives modified by various polycarboxylic acids; homopolymers of vinyl ether ester monomers and the like of polycarboxylic acids, or their copolymers with other common monomers, homopolymers of (meth)acrylic acid and the like, or their copolymer with other common monomers; homopolymers of  $\alpha,\beta$ -unsaturated vinyl monomers such as maleic anhydride and itaconic acid, and the like, or their copolymer with other common monomers; sulfonic acid-modified polymers obtained by modifying polyvinyl alcohol or a vinyl alcohol copolymer with a sulfonic acid compound; compounds having hydroxyl groups, such as ethylcellulose, benzylcellulose, hydroxyethylcellulose and hydroxypropylcellulose; etc. may be preferably used.

No particular limitation is imposed on the cationic compounds so far as they contain a cationic part in their molecules.

Examples of the cationic surfactants include quaternary ammonium salt type cationic surfactants such as monoalkylammonium chlorides, dialkylammonium chlorides, tetramethylammonium chloride, trimethylphenylammonium chloride and ethylene oxide-added ammonium chlorides; and amine salt type cationic surfactants. Amphoteric surfactants such as alkylbetaine, imidazolinium betaine and alanine type surfactants containing an cationic part may also be included.

Examples of the cationic polymers and oligomers include cationically modified products of polyacrylamide, copolymers of acrylamide with a cationic monomer, polyallylamine, polyamine-sulfone, polyvinylamine, polyethylene-imine, polyamide-epichlorohydrin resins and polyvinylpyridinium halides.

Homopolymers of vinylpyrrolidone type monomers or their copolymers with other common monomers; homopolymers of vinyloxazolidone type monomers or their copolymers with other common monomers; and homopolymers of vinylimidazole type monomers or their copolymers with other common monomers may also be included.

Examples of the common monomers include methacrylates, acrylates, acrylonitrile, vinyl ether, vinyl acetate, ethylene and styrene. Cationically modified polyvinyl alcohol, cellulose and the like may also be used. It goes without saying that the cationic substances are not limited to these surfactants and polymers or oligomers.

Examples of the pH adjustors include ammonia, various organic amines such as diethanolamine and triethanolamine, inorganic alkalizing agents such as alkali metal hydroxides such as sodium hydroxide, lithium hydroxide and potassium hydroxide, organic acids, and inorganic acids.

Two or more of these various compounds may be used at the same time.

In order to enhance the above function of the surface layer, as needed, various additives, for example, a surfactant, penetrant, crosslinking agent and/or the like, may be added to the surface layer.

A mixing ratio by weight of the resin particles to the binding agent is preferably within a range of from 1:2 to 50:1, more preferably from 3:1 to 20:1.

If the mixing ratio is lower than 1:2, the cracks or communicating pores in the resulting surface layer become small, so that its ink-absorbing effect is lessened. If the mixing ratio exceeds 50:1 on the other hand, the resin particles cannot be sufficiently bonded to each other and/or to the ink-retaining layer, resulting in a failure to form the surface layer.

The thickness of the surface layer may vary depending upon the quantity of ink droplets to be applied, but is preferably within a range of from 1 to 200  $\mu\text{m}$ , more preferably from 3 to 50  $\mu\text{m}$ .

The ink-retaining layer, which substantially captures the ink or printing agent therein, serves to absorb and capture the ink coming to pass through the surface layer, thereby substantially permanently retaining them therein.



The ink-retaining layer is required to have ink absorptivity stronger than that of the surface layer because if the absorptivity of the ink-retaining layer is weaker than that of the surface layer, the ink applied to the surface of the surface layer is partially retained in the surface layer at the time the ink passes through the surface layer, and the leading end of the ink reaches the ink-retaining layer, so that the ink penetrates and diffuses in a lateral direction of the surface layer at the interface between the surface layer and the ink-retaining layer. As a result, the resolving power of an image printed is reduced, resulting in a failure to form a high-quality image. The ink-retaining layer is also required to have good light transmitting properties because the image formed is viewed from the opposite side to the printing surface as described above.

The ink-retaining layer satisfying the above requirements is preferably composed of a light-transmitting cationic resin, which adsorbs the printing agent, and/or a light-transmitting hydrophilic resin having good solubility and swelling properties in the ink.

No particular limitation is imposed on the material for constructing the ink-retaining layer so far as it has a function of absorbing and capturing the ink and excellent transparency.

It is only necessary for the thickness of the ink-retaining layer to be sufficient to absorb and capture the ink. However, the thickness is preferably within a range of from 1 to 50  $\mu\text{m}$ , more preferably from 3 to 20  $\mu\text{m}$  though it may vary according to the quantity of ink droplets to be applied.

The pH of the ink-retaining surface is preferably not higher than 6, more preferably within a range of from 4 to 6. When the pH of the ink-retaining layer falls within this range, the pigment which has reached the ink-retaining layer undergoes moderate aggregation on the surface of the ink-retaining layer or in the interior thereof, so that an image which causes little bleeding and has excellent water fastness and moisture fastness can be formed.

If the desired pH cannot be achieved by only the above materials, the above-described various cationic or anionic surfactants, various cationic or anionic polymers or oligomers, and various pH adjusters may be used in combination.

As a process for forming the ink-retaining layer and the surface layer on the substrate, it is preferable to use a process in which the above-described respective materials are separately dispersed in a proper solvent to prepare coating formulations, and the coating formulations are applied to the substrate in that order by means of the conventionally-known method, for example, a roll coating, rod bar coating, spray coating or air knife coating process, and then quickly dried. A process in which the materials are applied by hot melt coating, or a process in which individual single sheets are formed from the materials, and the thus-formed sheets are laminated on the substrate may be used.

However, when the ink-receiving layer is provided on the substrate, it is necessary to firmly bond the substrate to the ink-retaining layer so as to annihilate space.

The presence of a space between the substrate and the ink-retaining layer is not preferred because irregular reflection occurs on the surface of a printed image, so that the optical density of a substantial image is reduced.

In the printing process according to the present invention, the printing surface and the viewing surface have an opposite relation to each other. When characters are printed, it is therefore necessary to use an apparatus capable of printing reflected-image characters unlike the conventional apparatus.

No particular limitation is imposed on the pigment inks for ink-jet used in the present invention. Outlines thereof will hereinafter be described.

The amount of a pigment contained in each of the pigment inks used in the present invention is preferably within a range of from 1 to 20 % by weight, preferably from 2 to 12 % by weight based on the total weight of the ink. Any pigments may be used in the present invention. As carbon black used in, for example, a black ink, there may be used those produced in accordance with the furnace process or channel process and having such properties that the primary particle diameter is within a range of from 15 to 40 nm, the specific surface area is within a range of from 50 to 300  $\text{m}^2/\text{g}$  as determined in accordance with the BET method, the oil absorption is within a range of from 40 to 150 ml/100 g as determined by using DBP, the volatile matter is within a range of from 0.5 to 10 %, and the pH is within a range of from 2 to 9. For example, commercially-available carbon black products such as No. 2300, No. 900, MCF 88, No. 33, No. 40, No. 45, No. 52, MA 7, MA 8 and No. 2200B (all, trade names, products of Mitsubishi Chemical Industries Limited), RAVEN 1255 (trade name, product of Columbian Carbon Japan Limited), REGAL 400R, REGAL 330R, REGAL 660R and MOGUL L (all, trade names, products of Cabot Company), and Color Black FW1, Color Black FW18, Color Black S170, Color Black S150, Printex 35 and Printex U (all, trade names, products of Degussa) may be used. As examples of pigments used in yellow, magenta and cyan inks, may be mentioned C.I. Pigment Yellow 1, C.I. Pigment Yellow 2, C.I. Pigment Yellow 3, C.I. Pigment Yellow 13, C.I. Pigment Yellow 16 and C.I. Pigment Yellow 83; C.I. Pigment Red 5, C.I. Pigment Red 7, C.I. Pigment Red 12, C.I. Pigment Red 48 (Ca), C.I. Pigment Red 48 (Mn), C.I. Pigment Red 57 (Ca), C.I. Pigment Red 112 and C.I. Pigment Red 122; and C.I. Pigment Blue 1, C.I. Pigment Blue 2, C.I. Pigment Blue 3, C.I. Pigment Blue 15:3, C.I. Pigment Blue 16, C.I. Pigment Blue 22, C.I. Vat Blue 4 and C.I. Vat Blue 6, respectively. However, the pigments are not limited to these pigments. It goes without saying that those newly prepared for the practice of the present invention may also be used in addition to the above pigments.

As a dispersant for the pigment contained in the ink used in the present invention, any resin may be used without any particular limitation so far as it is a water-soluble resin. However, those having a weight average molecular weight ranging from 1,000 to 30,000, more preferably from 3,000 to 15,000 may preferably be used. Specific examples of such

dispersants include block copolymers, random copolymers and graft copolymers composed of at least two monomers (at least one monomer being hydrophilic) selected from the group consisting of styrene, styrene derivatives, vinyl-naphthalene, vinyl-naphthalene derivatives, aliphatic alcohol esters of  $\alpha,\beta$ -ethylenically unsaturated carboxylic acids, acrylic acid, acrylic acid derivatives, maleic acid, maleic acid derivatives, itaconic acid, itaconic acid derivatives, fumaric acid, fumaric acid derivatives, and the like, and salts of these copolymers. These resins are alkali-soluble resins which dissolve in an aqueous solution of a base. Further, homopolymers composed of a hydrophilic monomer, or salts thereof may be used. It is also possible to use water-soluble resins such as polyvinyl alcohol, carboxymethylcellulose and naphthalenesulfonic acid-formaldehyde condensates.

Cationic dispersants such as acrylic copolymers containing monomer units composed of N,N-dimethylaminoethyl methacrylate, N,N-dimethylaminoethyl acrylate, N,N-dimethylaminomethacrylamide, N,N-dimethylaminopropylacrylamide, N,N-dimethylaminopropylmethacrylamide or the like, which has been quaternized with methyl chloride, dimethylsulfuric acid, benzyl chloride, epichlorohydrin or the like, may also be used.

It is desirable that the ink used in the present invention be adjusted to neutrality or alkalinity as the whole because the solubility of the water-soluble resin is enhanced, so that the ink can be provided as an ink far excellent in long-term storability. In this case, it is more desirable that the pH be adjusted to a range of from 7 to 10 because too high alkalinity forms the cause that various parts used in an ink-jet printing apparatus may be corroded.

The pigment and the water-soluble resin as described above are dispersed or dissolved in an aqueous medium.

An aqueous medium suitable for use in the inks used in the present invention is a mixed solvent of water and a water-soluble organic solvent. As the water, it is preferable to use ion-exchanged water such as deionized water instead of tap water containing various ions.

As examples of the water-soluble organic solvent used in combination with water, may be mentioned alkyl alcohols having 1 to 4 carbon atoms, such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol and tert-butyl alcohol; amides such as dimethylformamide and dimethylacetamide; ketones and keto-alcohols such as acetone and diacetone alcohol; ethers such as tetrahydrofuran and dioxane; polyalkylene glycols such as polyethylene glycol and polypropylene glycol; alkylene glycols the alkylene moiety of which has 2 to 6 carbon atoms, such as ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, thiodiglycol, hexylene glycol and diethylene glycol; 1,2,6-hexanetriol; glycerol; lower alkyl ethers of polyhydric alcohols, such as ethylene glycol monomethyl (or monoethyl) ether, diethylene glycol methyl (or ethyl) ether and triethylene glycol monomethyl (or monoethyl) ether; N-methyl-2-pyrrolidone; 2-pyrrolidone; and 1,3-dimethyl-2-imidazolidinone.

The content of the water-soluble organic solvent in the ink used in the present invention is generally within a range of from 3 to 50 %, preferably from 3 to 40 % by weight based on the total weight of the ink, while the content of water used is within a range of from 10 to 90 % by weight, preferably from 30 to 80 % by weight based on the total weight of the ink.

Each of the inks used in the present invention is prepared in the following manner. The pigment is first added to an aqueous solution containing at least the water-soluble resin as a dispersant and water, and the mixture is stirred. A dispersion treatment is then conducted in accordance with a dispersing means described below, and as needed, a centrifugation is carried out to obtain a desired dispersion. Optional additive components usable in the present invention are then added to the dispersion, and the resultant mixture is stirred to prepare an ink.

It is more effective to conduct premixing for at least 30 minutes before the aqueous solution containing the pigment is subjected to the dispersion treatment. This premixing serves to improve the wettability of the surface of the pigment and facilitate adsorption of the dispersant on the pigment surface.

Any dispersing machine commonly used may be employed as a dispersing machine used in the present invention. As examples thereof, may be mentioned ball mills, roll mills and sand mills.

Of these mills, a high-speed sand mill may preferably be used. Examples thereof include Super Mill, Sand Grinder, Beads Mill, Agitator Mill, Grain Mill, Dyno Mill, Pearl Mill and Coball Mill (all, trade names).

As methods for obtaining a pigment having a desired particle size distribution, may be mentioned techniques in which the size of a grinding medium in a dispersing machine is made smaller, in which the packing rate of a grinding medium is made higher, in which processing time is made longer, in which discharging rate is made lower, and in which classification is conducted by filter, centrifugal separator or the like after grinding. Any combination thereof may also be included.

The average particle diameter of the pigment particles in the pigment inks used in the present invention is within a range of from 100 to 500 nm, preferably from 100 to 200 nm in terms of aggregates of primary particles. The average particle diameter of the pigment particles can be measured by any conventionally-known method such as a centrifugal precipitation method, X-ray transmission method, laser diffraction method or sieving method.

An illustrative example of an ink-jet printing apparatus, which is suitable for use in conducting printing with the printing medium according to the present invention, will hereinafter be described. Examples of the construction of a head, which is a main part of such an apparatus, are illustrated in Figs. 1, 2 and 3. Referring now to Fig. 1, a head 13 is formed by bonding a glass, ceramic or plastic plate or the like having a groove 14 through which an ink is passed, to a heating head 15, which is used for thermal recording (the drawings show a head to which, however, the invention is not limited).



The heating head 15 is composed of a protective film 16 made of silicon oxide or the like, aluminum electrodes 17-1 and 17-2, a heating resistor layer 18 made of nichrome or the like, a heat accumulating layer 19, and a substrate 20 made of alumina or the like having a good heat radiating property. An ink 21 comes up to an ejection orifice (a minute opening) 22 and forms a meniscus 23 due to a pressure P.

Now, upon application of electric signals to the electrodes 17-1 and 17-2, the heating head 15 rapidly generates heat at the region shown by n to form bubbles in the ink 21 which is in contact with this region. The meniscus 23 of the ink is projected by the action of the pressure thus produced, and the ink 21 is ejected from the orifice 22 to a printing medium 25 in the form of minute droplets 24. Fig. 3 illustrates an appearance of a multi-head composed of an array of a number of heads as shown in Fig. 1. The multi-head is formed by closely bonding a glass plate 27 having a number of grooves 26 to a heating head 28 similar to the head as illustrated in Fig. 1.

Incidentally, Fig. 1 is a cross-sectional view of the printing head 13 taken along the flow path of ink, and Fig. 2 is a cross-sectional view taken along line 2-2 in Fig. 1.

Fig. 4 illustrates an example of an ink-jet printing apparatus in which such a head has been incorporated. In Fig. 4, reference numeral 61 designates a blade serving as a wiping member, one end of which is a stationary end held by a blade-holding member to form a cantilever. The blade 61 is provided at a position adjacent to a region in which a printing head operates, and in this embodiment, is held in such a form that it protrudes into the course through which the printing head is moved. Reference numeral 62 indicates a cap, which is provided at a home position adjacent to the blade 61, and is so constructed that it moves in a direction perpendicular to a direction in which the printing head is moved, and comes into contact with the face of ejecting openings to cap it. Reference numeral 63 denotes an ink-absorbing member provided adjointly to the blade 61 and, similar to the blade 61, held in such a form that it protrudes into the course through which the printing head is moved. The above-described blade 61, cap 62 and absorbing member 63 constitute an ejection-recovery portion 64, where the blade 61 and absorbing member 63 remove water, dust and/or the like from the face of the ink-ejecting openings.

Reference numeral 65 designates the printing head having an ejection-energy-generating means and serving to eject the ink onto a printing medium set in an opposing relation to the ejection opening face provided with the ejection openings to conduct printing. Reference numeral 66 indicates a carriage on which the printing head 65 is mounted so that the printing head 65 can be moved. The carriage 66 is slidably interlocked with a guide rod 67 and is connected (not illustrated) at its part to a belt 69 driven by a motor 68. Thus, the carriage 66 can be moved along the guide rod 67 and hence, the printing head 65 can be moved from a printing region to a region adjacent thereto.

Reference numerals 51 and 52 denote a feeding part from which the printing media are separately inserted, and feed rollers driven by a motor (not illustrated), respectively. With such a construction, the printing medium is fed to the position opposite to the ejection opening face of the printing head 65, and discharged from a discharge section provided with discharge rollers 53 with the progress of printing.

In the above construction, the cap 62 in the head recovery portion 64 is receded from the path of motion of the printing head 65 when the printing head 65 is returned to its home position, for example, after completion of printing, and the blade 61 remains protruded into the path of motion. As a result, the ejection opening face of the printing head 65 is wiped. When the cap 62 comes into contact with the ejection opening face of the printing head 65 to cap it, the cap 62 is moved so as to protrude into the path of motion of the printing head 65.

When the printing head 65 is moved from its home position to the position at which printing is started, the cap 62 and the blade 61 are at the same positions as the positions for the wiping as described above. As a result, the ejection opening face of the printing head 65 is also wiped at the time of this movement.

The above movement of the printing head 65 to its home position is made not only when the printing is completed or the printing head is recovered for ejection, but also when the printing head 65 is moved between printing regions for the purpose of printing, during which it is moved to the home position adjacent to each printing region at given intervals, where the ejection opening face is wiped in accordance with this movement.

The present invention will hereinafter be described more detail by the following examples. Incidentally, all designations of "part" or "parts" and "%" as will be used in the following examples mean part or parts by weight and % by weight unless expressly noted.



**Example 1:****[Preparation of pigment dispersion]**

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Styrene-acrylic acid-ethyl acrylate copolymer (acid value: 140, weight average molecular weight: 5,000)	1.5 parts
Ethanolamine	1 part
Deionized water	81.5 parts
Diethylene glycol	5 parts.

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The above components were mixed and heated to 70°C in a water bath to completely dissolve the resin component therein. To this solution, were added 10 parts of C.I. Pigment Red 112 and 1 part of isopropyl alcohol to premix them for 30 minutes. Thereafter, the resultant premix was subjected to a dispersion treatment under the following conditions:

- 20 Dispersing machine: Sand Grinder (trade name, manufactured by Igarashi Kikai K.K.)  
 Grinding medium: zirconium beads (diameter: 1 mm) Packing rate of the grinding medium: 50 % (by volume)  
 Grinding time: 3 hours.

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The dispersion was further subjected to a centrifugal treatment (12,000 rpm, 20 minutes) to remove coarse particles into a dispersion.

**[Preparation of magenta ink]**

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Dispersion described above	30 parts
Glycerol	10 parts
Ethylene glycol	5 parts
N-Methylpyrrolidone	5 parts
Ethyl alcohol	2 parts
Acetylenol EH (trade name, product of Kawaken Fine Chemicals Co., Ltd.)	0.2 part
Deionized water	47.8 parts.

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The above components were mixed to prepare a pigment ink of a magenta color.

The average particle diameter of the pigment particles in the ink was measured by a coulter counter and was found to be 120 nm.

A stable pH region to this pigment ink was 7.2 or higher.

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Incidentally, the stable pH region to the pigment ink was determined by changing the pH of the pigment ink kept in a good dispersion state using monoethanolamine and hydrochloric acid to measure a pH region in which the pigment neither precipitated nor aggregated.

**[Preparation of cyan ink]**

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A pigment ink of a cyan color was prepared in exactly the same manner as in the magenta ink except that the pigment was changed to C.I. Pigment Blue 22. A stable pH region as determined in the same manner as described above was 7.4 or higher.

The average particle diameter of the pigment particles in the ink was measured by a coulter counter and was found to be 130 nm.

## [Preparation of yellow ink]

A pigment ink of a yellow color was prepared in exactly the same manner as in the magenta ink except that the pigment was changed to C.I. Pigment Yellow 13. A stable pH region as determined in the same manner as described above was 8.0 or higher.

The average particle diameter of the pigment particles in the ink was measured by a coulter counter and was found to be 125 nm.

## [Preparation of black ink]

A pigment ink of a black color was prepared in exactly the same manner as in the magenta ink except that the pigment was changed to carbon black (MCF 88, trade name, product of Mitsubishi Chemical Industries Limited).

The average particle diameter of the pigment particles in the ink was measured by a coulter counter and was found to be 100 nm. A stable pH region as determined in the same manner as described above was 7.8 or higher.

## [Production of Printing Medium 1]

A polyethylene terephthalate film (thickness: 100  $\mu\text{m}$ , product of Toray Industries, Inc.) was used as a light-transmitting base material, coated with the following composition A by a bar coater process so as to give a dry coating thickness of 8  $\mu\text{m}$ , and then dried at 120°C for 5 minutes in a drying oven.

## Composition A:

Polyvinyl pyrrolidone (PVPK-90, trade name, product of GAF Corp., 10 % DMF solution)	78 parts
Novolak type phenol resin (Resitop PSK-2320, trade name, product of Gun-ei Chemical Industry Co., Ltd., 10 % DMF solution)	12 parts
Polyallylamine hydrochloride (PAA-HCl, product of Nitto Boseki Co., Ltd.).	10 parts

Further, the following composition B was applied onto the thus-formed coating layer by the bar coater process so as to give a dry coating thickness of 15  $\mu\text{m}$ , and then dried at 80°C for 10 minutes in the drying oven. The pH of the resultant layer was 5.4.

## Composition B:

Fine powder of silicone resin (Tospearl 120, trade name, product of Toshiba Silicone Co., Ltd., particle diameter: 2 $\mu\text{m}$ )	100 parts
Ethylene-vinyl acetate copolymer resin (Chemipearl V-100, trade name, product of Mitsui Petrochemical Industries, Ltd., solids content: 40 %, particle diameter: 5 $\mu\text{m}$ )	10 parts
Sodium polycarbonate type surfactant (Demol EP, trade name, product of Kao Corporation).	1 part

The thus-obtained printing medium was white-opaque. The pH of the resultant surface layer was 8.3.

Example 2:

The same polyethylene terephthalate film as that used in Example 1 was used as a light-transmitting base material, coated with the following composition C by a bar coater process so as to give a dry coating thickness of 5  $\mu\text{m}$ , and then dried at 110°C for 10 minutes in a drying oven.

## Composition C:

5	Polyvinyl pyrrolidone (PVPK-90, trade name, product of GAF Corp., 10 % DMF solution)	74 parts
	Styrene-acrylic acid copolymer (Oxylac SH-2100, trade name, product of Nippon Shokubai Kagaku Kogyo Co., Ltd., 10 % DMF solution)	16 parts
10	Polyallylamine hydrochloride (PAA-HCl, product of Nitto Boseki Co., Ltd.).	10 parts

Further, the following composition D was applied onto the thus-formed coating layer by the bar coater process so as to give a dry coating thickness of 20  $\mu\text{m}$ , and then dried at 80°C for 10 minutes in the drying oven. The pH of the resultant layer was 4.6.

## Composition D:

20	Benzoguanamine resin (Epostar M, trade name, product of Nippon Shokubai Kagaku Kogyo Co., Ltd., particle diameter: 1 to 2 $\mu\text{m}$ )	100 parts
	Ionomer resin (Chemipearl SA100, trade name, product of Mitsui Petrochemical Industries, Ltd., solids content: 35 %)	30 parts
25	Sodium sulfodiphenyl ether (Pelex SS-H, trade name, product of Kao Corporation)	2 parts
	Water	20 parts.

The thus-obtained printing medium was white-opaque. The pH of the resultant surface layer was 8.2.

Example 3:

The same polyethylene terephthalate film as that used in Example 1 was used as a light-transmitting base material, coated with the following composition E, to which acetic acid had been added to adjust its pH to 5.8, by a bar coater process so as to give a dry coating thickness of 10  $\mu\text{m}$ , and then dried at 100°C for 12 minutes in a drying oven.

## Composition E:

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45	Comb type polymer* (LHM-108, trade name, product of Soken Chemical & Engineering Co., Ltd., 25 % methyl cellosolve solution)	60 parts
	Methyl vinyl ether/maleic anhydride monoethyl ester (Ganterz EZ-425, trade name, product of GAF Corp., 10 % water/ethanol solution)	40 parts

\*: Obtained by graft-polymerizing 20 parts of MMA on 80 parts of a backbone (a copolymer of 64 parts of 2-hydroxyethyl methacrylate and 16 parts of dimethylacrylamide).

Further, the following composition F was applied onto the thus-formed coating layer by the bar coater process so as to give a dry coating thickness of 10  $\mu\text{m}$ , and then dried at 70°C for 10 minutes in the drying oven.



## Composition F:

5	Crosslinked polymethyl methacrylate (Microsphere M-305, trade name, product of Matsumoto Yushi-Seiyaku Co., Ltd., particle diameter: 10 to 12 $\mu\text{m}$ )	100 parts
	Ionomer resin (Chemiparl SA100, trade name, product of Mitsui Petrochemical Industries, Ltd., solids content: 35 %)	10 parts
10	Sodium alkylbenzenesulfonate (Neopelex, trade name, product of Kao Corporation).	1.5 parts

The thus-obtained printing medium was white-opaque. The pH of the resultant surface layer was 8.7.

Example 4:

A white-opaque printing medium was obtained in exactly the same manner as in Example 3 except that the crosslinked polymethyl methacrylate in the composition F used in Example 3 was changed to a benzoguanamine resin (Epostar S, trade name, product of Nippon Shokubai Kagaku Kogyo Co., Ltd., particle diameter: 0.3  $\mu\text{m}$ ). The pH of the resultant surface layer was 8.6.

Example 5:

After the same compositions E and F as those used in Example 3 were applied onto a Teflon film in the same manner as in Example 3, the Teflon film was separated, thereby obtaining a white-opaque printing medium.

Comparative Example 1:

The same polyethylene terephthalate film as that used in Example 1 was used as a light-transmitting base material, coated with the following composition G by a bar coater process so as to give a dry coating thickness of 6  $\mu\text{m}$ , and then dried at 120°C for 5 minutes in a drying oven.

## Composition G:

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Cationically modified polyvinyl alcohol (C-Polymer, trade name, product of Kuraray Co., Ltd., 10 % aqueous solution)	100 parts
Blocked polyisocyanate (Elaston BN-5, trade name, product of Dai-ichi Kogyo Seiyaku Co., Ltd., solids content: 30 %).	3 parts

Further, the following composition H was applied onto the thus-formed coating layer by the bar coater process so as to give a dry coating thickness of 25  $\mu\text{m}$ , and then dried at 80°C for 10 minutes in the drying oven.

## Composition H:

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Urea-formalin resin (organic filler, product of Nippon Kasei Chemical Co., Ltd., primary particle diameter: 0.01 to 0.02 $\mu\text{m}$ )	100 parts
Acetalated polyvinyl alcohol (S-lec KX-1, trade name, product of Sekisui Chemical, Co., Ltd., non-volatile content: 8 %)	500 parts
Perfluoroalkylbetaine (Surflon S-131, trade name, Seimi Chemical Co., Ltd., solids content: 30 %).	0.3 part

The thus-obtained printing medium was white-opaque.

### Comparative Example 2:

A white-opaque printing medium was obtained in exactly the same manner as in Comparative Example 1 except that the urea-formalin resin in the composition H used in Comparative Example 1 was changed to synthetic silica (Sylysia, trade name, product of Fuji Silysia K.K., primary particle diameter: 0.02 to 0.03  $\mu\text{m}$ ).

The pore diameter distributions of the printing media obtained above were determined by means of a mercury intrusion porosimeter. The results are shown in Table 1.

Using the inks having the above-described respective compositions, printing was conducted on each of the printing media under the following conditions by means of an ink-jet printing apparatus in which an ink is ejected from an orifice by bubbling of the ink by thermal energy, thereby evaluating the printing media as to the following item.

Printing conditions:

Ejection frequency:	4 kHz
Volume of ejection droplet:	45 pl
Printing density:	360 DPI
Maximum printing density of a single color ink:	8 nl/mm <sup>2</sup> .

Evaluated item:

(1) Optical density:

The optical density of a solid printed area of a magenta (M) color as to each print sample obtained by conducting solid printing (100 % duty) by means of the above printer was measured by means of a Macbeth Densitometer RD-918 from the side of the light-transmitting base material.

The evaluation results are shown collectively in Table 1.

Table 1

	Diameter at peak not greater than 100 nm in a pore diameter distribution curve [nm]	Pore volume of pores corresponding to the peak [cc/g]	Diameter at peak greater than 100 nm in a pore diameter distribution curve [nm]	Pore volume of pores corresponding to the peak [cc/g]	Optical density
Ex. 1	85	0.007	2100	0.082	1.51
Ex. 2	80	0.009	1700	0.085	1.50
Ex. 3	91	0.004	10800	0.090	1.52
Ex. 4	72	0.010	340	0.075	1.49
Ex. 5	93	0.003	11200	0.077	1.51
Comp. Ex. 1	15	0.070	104	0.004	1.18
Comp. Ex. 2	23	0.062	121	0.003	1.21
Note: When plural peaks are present, the value of a peak at which the pore volume is the greatest is shown.					

According to the present invention, as described above, it is possible to perform an ink-jet printing process, which can provide images having high optical density and excellent coloring, by using the printing medium comprising a sur-

face layer having liquid permeability and an ink-retaining layer, in which the printing surface and the viewing surface have an opposite relation to each other, and pigment inks which each comprise pigment particles having a particle diameter within a specified range and develop fastness properties such as water fastness and light fastness, said printing medium having peaks in a pore diameter distribution curve, which correspond to the particle diameter of the pigment particles.

While the present invention has been described with respect to what is presently considered to be the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. To the contrary, the invention is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims. The scope of the following claims is to be accorded to the broadest interpretation so as to encompass all such modifications and equivalent structures and functions.

Disclosed herein is a printing medium comprising a surface layer having liquid permeability and an ink-retaining layer, wherein a pore volume of pores corresponding to a peak not greater than 100 nm in a pore diameter distribution curve of the printing medium is at most 0.015 cc/g, a pore volume of pores corresponding to at least one of peaks greater than 100 nm is at least 0.015 cc/g, and the pH of the surface layer is at least 8.

## Claims

1. A printing medium comprising a surface layer having liquid permeability and an ink-retaining layer, wherein a pore volume of pores corresponding to a peak not greater than 100 nm in a pore diameter distribution curve of the printing medium is at most 0.015 cc/g, a pore volume of pores corresponding to at least one of peaks greater than 100 nm is at least 0.015 cc/g, and the pH of the surface layer is at least 8.
2. The printing medium according to Claim 1, wherein the pH of the ink-retaining layer is at most 6.
3. The printing medium according to Claim 1, wherein the ink-retaining layer and the surface layer are laminated on a base material.
4. The printing medium according to Claim 1, wherein the base material has good light transmitting properties.
5. The printing medium according to Claim 1, wherein the surface layer is porous.
6. The printing medium according to Claim 1, wherein the surface layer is composed principally of resin particles and a binding agent.
7. The printing medium according to Claim 1, wherein the ink-retaining layer is transparent.
8. The printing medium according to Claim 1, wherein the ink-retaining layer is composed principally of a cationic resin and/or a hydrophilic polymer.
9. The printing medium according to Claim 1, wherein the surface layer has good light diffusing properties, and the ink-retaining layer has better light transmitting properties than the surface layer.
10. The printing medium according to Claim 1, wherein the ink-retaining layer has stronger ink absorptivity than the surface layer.
11. The printing medium according to Claim 1, wherein the surface layer has communicating pores.
12. The printing medium according to Claim 1, wherein the surface layer has cracks therein.
13. A printing process comprising ejecting inks, which each comprise pigment particles having an average particle diameter within a range of from 100 nm to 500 nm, from ejection orifices in response to printing signals to apply the inks in the form of droplets to the printing medium according to any one of Claims 1 to 12.
14. The printing process according to Claim 13, wherein the inks are applied to the surface layer of the printing medium, thereby making printing.
15. The printing process according to Claim 13, wherein four inks of yellow, magenta, cyan and black colors are used as the inks.



16. The printing process according to Claim 13, wherein the inks are applied by an ink-jet system.

17. The printing process according to Claim 16, wherein the ink-jet system is a system in which thermal energy is applied to an ink to eject the ink.

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18. The printing process according to Claim 13, wherein the diameter of pores corresponding to the peak greater than 100 nm in the pore diameter distribution curve of the printing medium is greater than an average particle diameter of an aggregated particle of the pigment in each ink.

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19. The printing process according to Claim 13, wherein the pH of the surface layer of the printing medium is equal to or higher than a pH within a stable pH region to each pigment ink.

20. The printing process according to Claim 13, wherein the pH of the ink-retaining layer of the printing medium is lower than any pH within a stable pH region to each pigment ink.

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21. A process of producing a print, comprising applying inks, which each comprise pigment particles having an average particle diameter within a range of from 100 nm to 500 nm, to the surface layer of the printing medium according to any one of Claims 1 to 12 by an ink-jet system, thereby forming an image on the ink-retaining layer through the surface layer.

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22. The process according to Claim 21, wherein the ink-jet system is a system in which thermal energy is applied to an ink to eject the ink.

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FIG. 1

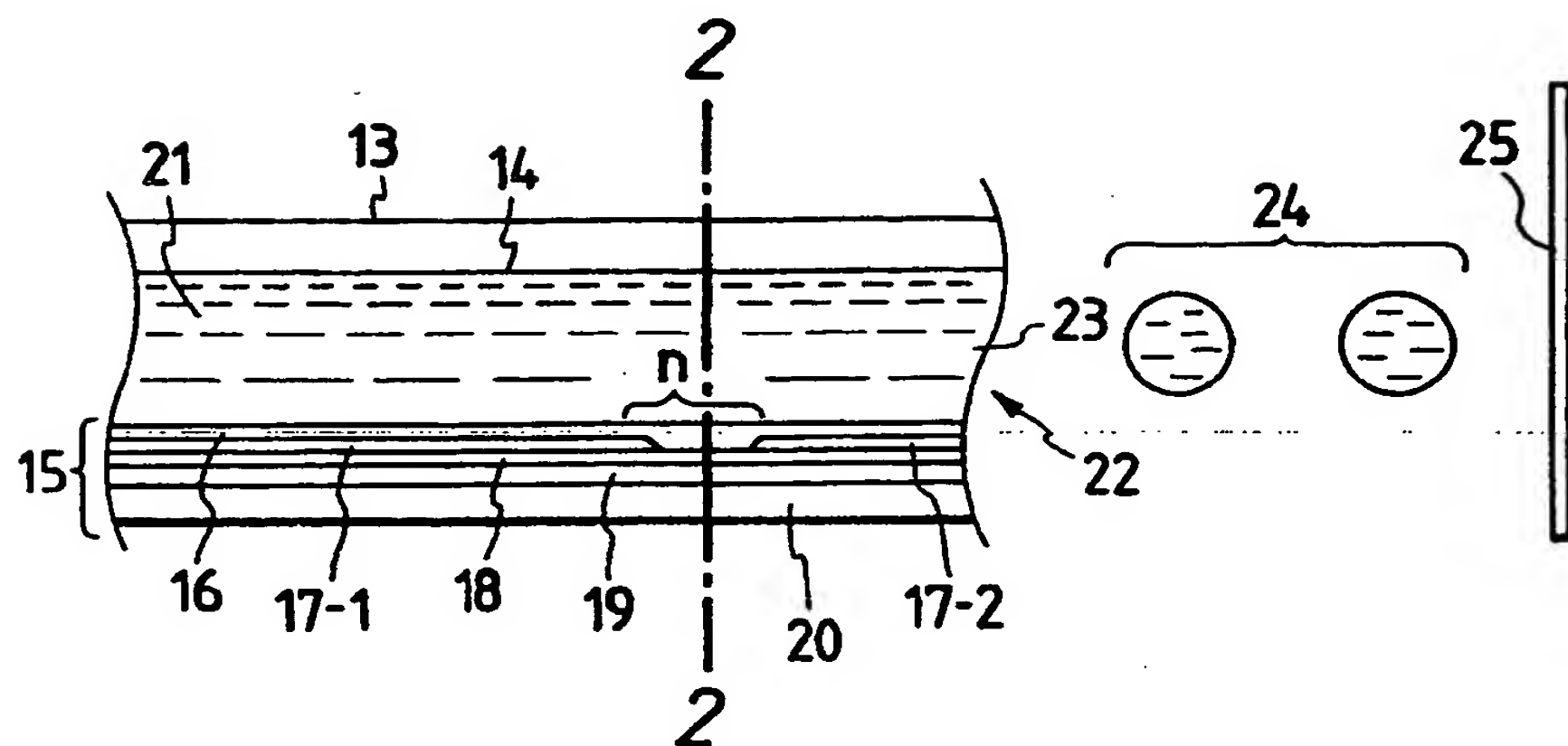


FIG. 2

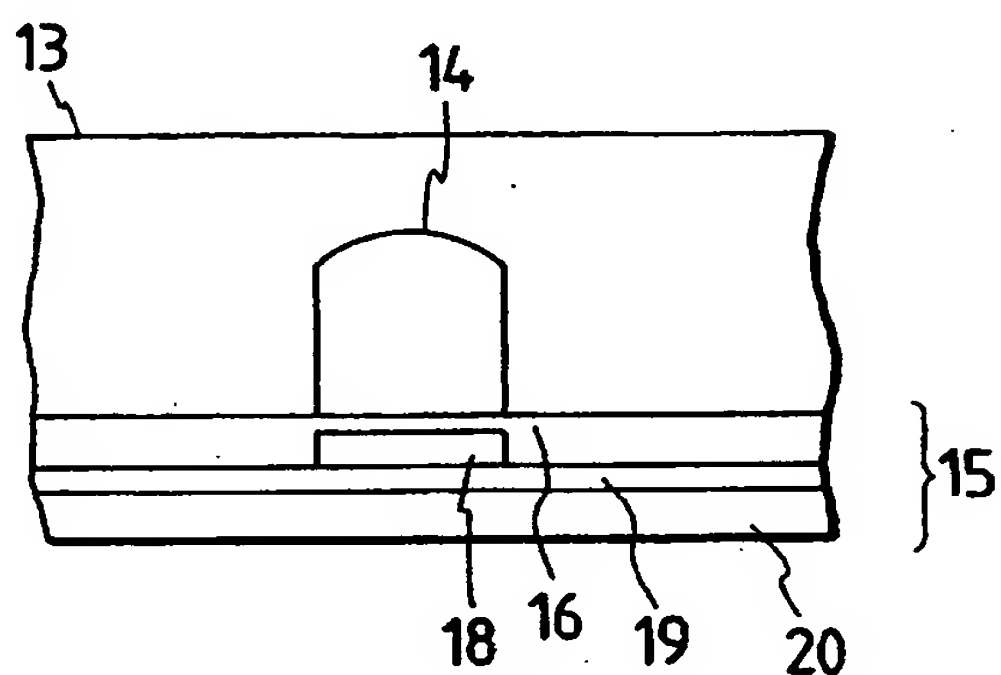
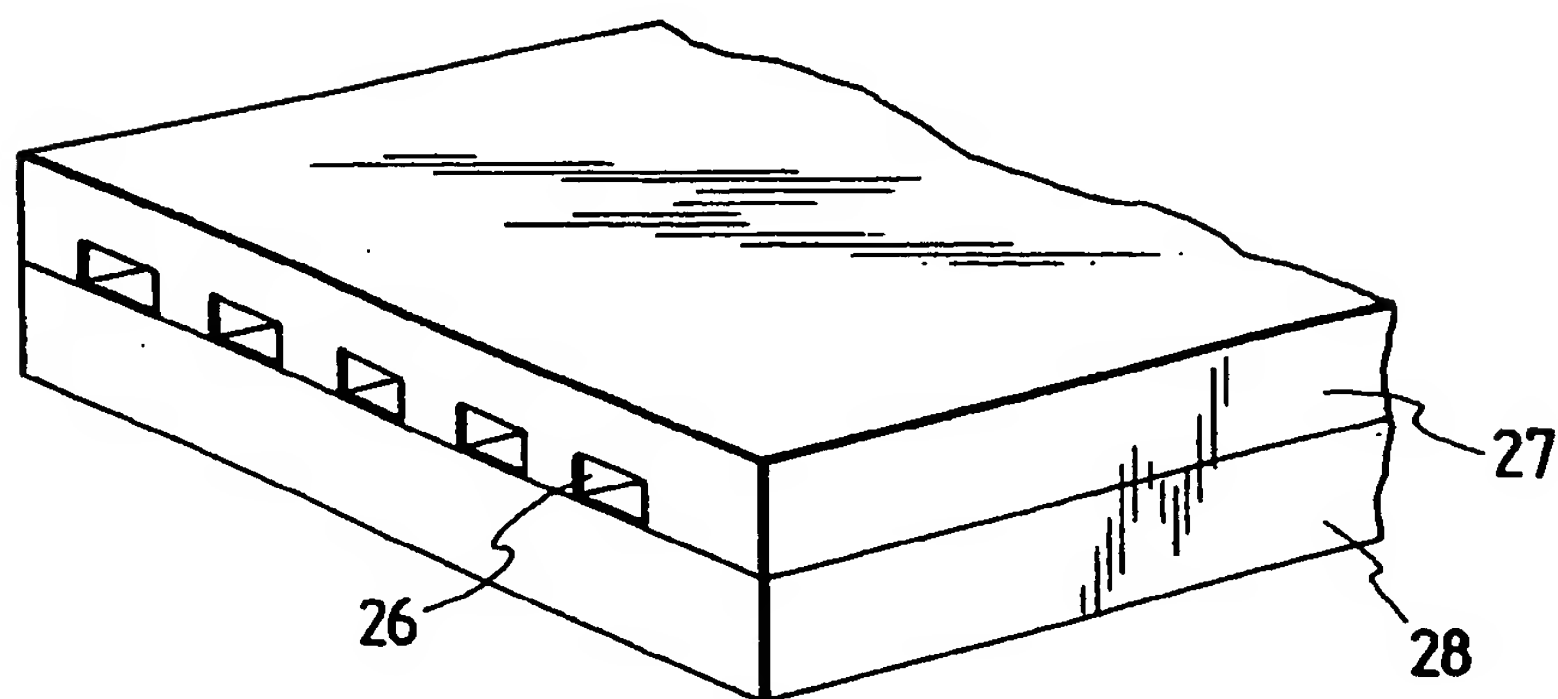
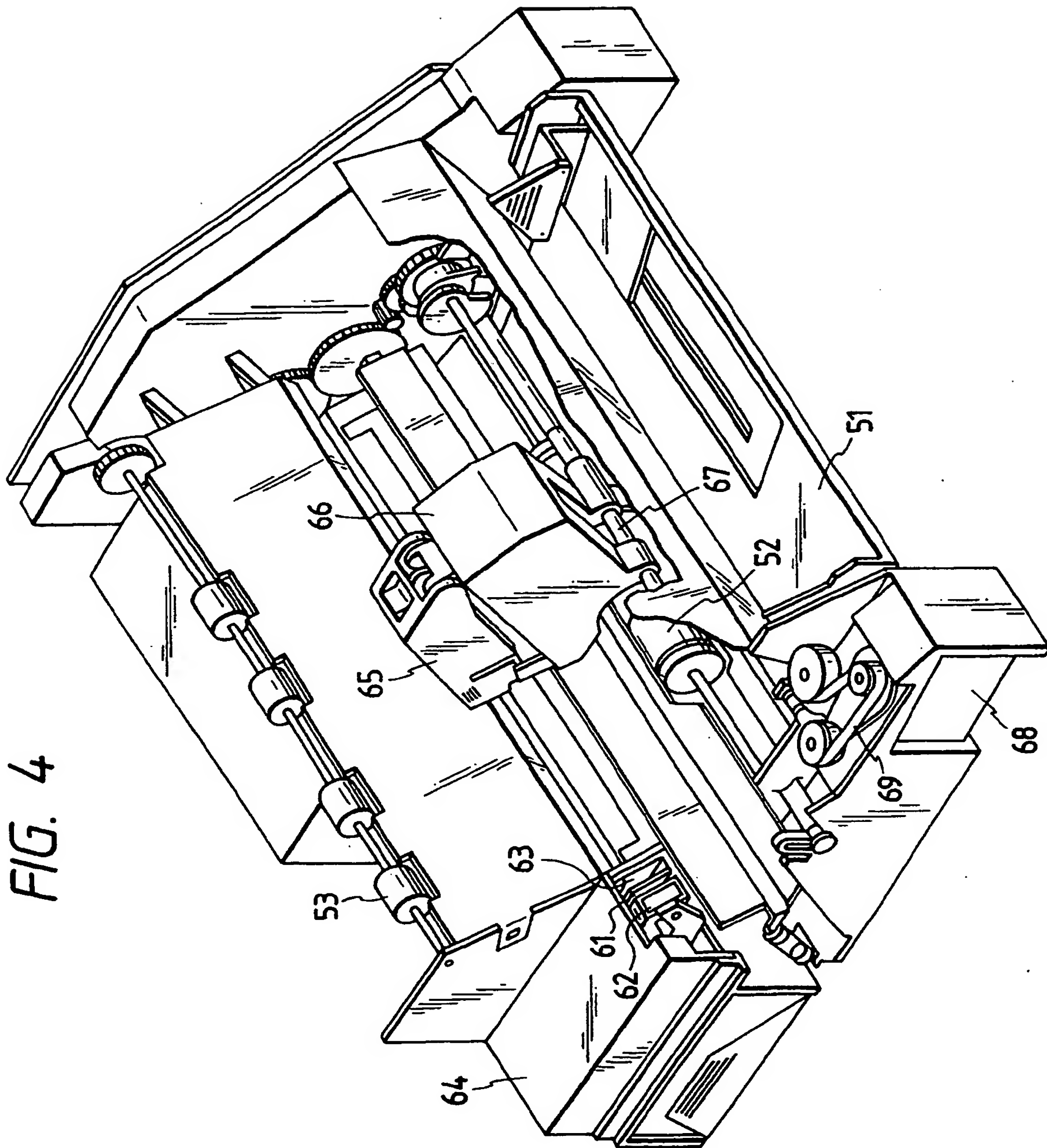


FIG. 3









European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 96 10 7934

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,A	US-A-4 785 313 (M HIGUMA) * the whole document *	1	B41M5/00
A	US-A-4 460 637 (S MIYAMOTO) * the whole document *	1	
A	EP-A-0 622 244 (CANON) * the whole document *	1	
A	EP-A-0 636 489 (CANON) * the whole document *	1	
The present search report has been drawn up for all claims			<b>TECHNICAL FIELDS SEARCHED (Int.Cl.6)</b>  B41M
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>9 September 1996</b>	Examiner <b>Heywood, C</b>
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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